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Chapter 21. Nuclear Forensics in Radiometric Methods of Detection

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Chapter 21.
Nuclear Forensics

in

Radiometric Methods of Detection

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Abstract

Nuclear forensics, the analysis of interdicted nuclear material to provide information for both law enforcement and national intelligence, remains an area of active interest for both scientists and public policy experts.   From the technical perspective, nuclear forensics requires expertise in the analysis of nuclear materials, as well as expertise in the characteristics imparted on those materials by manufacturing processes in the civilian and military nuclear fuel cycles. Radiometric analysis techniques play a significant role in analyzing these interdicted materials, providing a means for both quick, non-destructive analysis of the material in the field, as well as highly sensitive analyses for short- and medium-lived isotopes in the laboratory. Nuclear forensic analysis also utilizes non-radiometric materials analysis techniques, as well conventional forensic techniques.   This chapter will describe the field of nuclear forensics, working from the national objective for nuclear attribution to the underlying requirements for validated signatures and high-quality analytical results using a variety of materials analysis techniques. Examples from real interdicted materials, as well as international exercise, will be used to demonstrate the key concepts of nuclear forensics.

Introduction

What is Nuclear Forensics?

The field of nuclear forensics has been a topic of intense discussion in the scientific literature (1-4), the public policy literature (5-8), and the popular press (9-12) since at least 2003. **Nuclear forensics** has been defined as:

> the analysis of intercepted illicit nuclear or radioactive material and any associated material to provide evidence for nuclear attribution. The goal of nuclear forensics analysis is to identify forensic indicators in interdicted nuclear and radiological samples or the surrounding environment, e.g., the container or transport vehicle. These indicators arise from known relationships between material characteristics and process history (13).

The "analysis" in the definition above includes, but is by no means limited to, radiometric measurement techniques. This chapter will describe the entire field of nuclear forensics, including both radiometric and non-radiometric techniques, but emphasizing the role of radiometric measurements as they are encountered.

The Origins of Nuclear Forensics

It is impossible to define a birth date for nuclear forensics, since many of the techniques and methods used in nuclear forensics have deep roots in the U.S. nuclear weapons program. However, the field rose to some prominence with the rash of interdictions of nuclear material following the break-up of the Soviet Union in 1992. According to the IAEA's Illicit Trafficking Database (14), there were at least 11 major seizures of highly enriched uranium (HEU) or plutonium from 1992 through 1996, primarily in Russia and Europe. In response, the first organizational meeting of what was to become the Nuclear Forensics International Technical Working Group (ITWG), a group that offers technical solutions in nuclear forensics to requesting countries, was held at Lawrence Livermore National Laboratory (LLNL) in 1995. The ITWG was chartered by the G-8 in 1996, and still reports informally to the G-8 Nuclear Safety and Security Group, although the ITWG includes representatives from countries around the world (15-16). Even with these initial efforts, the field held little general interest for many years and was primarily the province of a few hardy pioneers at laboratories such as LLNL, the Institute for Transuranium Elements (ITU) in Karlsruhe, Germany, the Centre L'Energie Atomique (CEA) in France, the United Kingdom Atomic Weapons Establishment (AWE), and others.

The terrorist attacks on New York City and Washington, DC, on September 11, 2001, greatly increased the visibility of nuclear forensics, as policy makers became increasingly worried about the possibility of well-organized terrorist groups, such as Al Qaeda, obtaining a nuclear weapon or using a radiological dispersal device (RDD or so-called "dirty bomb"). Thus, began a significant increase in funding for nuclear security, including nuclear forensics, in the United States, but also in other countries. At the same time, the U.S. government began to grapple with how to best organize and execute a mission which inherently has both research and operational components.

The Policy Implications of Nuclear Forensics

The basic problem of nuclear forensics is how to apply modern materials analysis techniques, knowledge of both commercial and military nuclear fuel cycles, and scientific principles to analyze unknown nuclear materials or devices and provide information of value to decision-makers. This problem is complex enough before one considers the wide range of potential materials and devices that might be encountered and the many different types of information that might be required.

When considering the full range of materials to be addressed by a nuclear forensics program, one must consider not only the full range of uranium and plutonium materials from the civilian and military nuclear fuel cycles, from uranium ore to reactor fuel or even weapon parts, but also highly radioactive materials that might be dispersed in an RDD, e.g., irradiated fuel rods and separated isotopes for medical or other purposes.

When considering the different types of information that might be required, one must think not only about the information needs of law enforcement, but also that of national intelligence. Nuclear forensics has had a strong law-enforcement focus from the very beginning, because the initial driving force behind the field was the ongoing interdiction of illicit nuclear material in Russia and Europe. In general, these interdictions were made by law enforcement or border personnel and the ultimate goal was bringing each case to a successful prosecution. However, although the standards for admissibility of evidence are often quite high, the specific nuclear forensic results brought before a court of law are often quite few. Since, in most cases to date, the perpetrators were caught with the material in hand, it was only necessary to prove that the material was indeed illegal. In the simplest cases, one might only need to know the basic chemical identity of the material, its mass (to prove that it exceeds some *de minimis* threshold), and enrichment level (for uranium).

National intelligence, which certainly includes law enforcement intelligence as well as nuclear intelligence, seeks to know more about the material: Where did it come from? What was its intended purpose? Where was legitimate control lost? What smuggling groups or routes were involved in moving the material? Providing this type of information requires much more sophisticated analysis and interpretation, yet the standards of evidence, while probably not as formal as those of law enforcement, must nonetheless be equally as high, because, while the legal system has courts of appeals to overturn bad decisions, some actions taken by national leaders based upon such intelligence information have no such courts of appeals.

The U.S. government has divided nuclear forensics into 3 mission areas: interdicted pre-detonation materials, interdicted nuclear devices, and post-detonation (17). However, the mission areas of nuclear forensics of interdicted nuclear devices and post-detonation debris are intimately tied to the design and construction of nuclear weapons, information at least sensitive, if not classified. Therefore, this chapter will devote itself to pre-detonation nuclear forensics of interdicted materials, except to note that post-detonation debris will be highly radioactive, with many short- to medium-lived fission and activation products. So, one should expect that radiometric methods of analysis will play a large part in the field of post-detonation forensics.

How the Case Begins

A nuclear forensic case can begin in many ways (see Table 1). Some cases begin quite simply with the discovery of unknown material, apparently lost or abandoned by its rightful owner, such as the discovery of HEU in the basement of a bank in Vilnius, Lithuania, in 1993 (18). Police investigations, instigated either as a result of a known theft, a tip-off, or a sting operation have also been a significant source of nuclear materials seizures (18-23). The traffickers are often caught as they seek to find a buyer for their material and unwittingly contact undercover law enforcement instead. On the other hand, the seizure of highly enriched uranium oxide in Rousse, Bulgaria, in 1999 was effected by border guards who correctly judged that Ozcan Hanifi fit the profile of a smuggler (24-25). Many countries around the world have now erected large networks of passive detectors to prevent or detect the unauthorized movement of nuclear material. Although the majority of interdictions took place in the 1990's, following the fall of the Soviet Union, we can find evidence in the literature of nuclear forensic analysis of interdicted materials as far back as 1978 (26) and we also have a number of recent interdictions, such as the interdictions of HEU in Georgia in 2003, 2006, and 2010, which were widely reported in the popular press (27-31).

Figure 1

HEU oxide sample alongside its lead container ("pig")
interdicted in Rousse, Bulgaria, in 1999.
Reproduced from (24).

For all of these cases, the nuclear material is usually neatly packaged, ready for seizure by law enforcement personnel and transport to the nuclear forensics laboratory. Such cases call for an

operational response, as defined in IAEA TECDOC -1313 (32). However, one must also be prepared for the messier case in which the nuclear material might have been intentionally or inadvertently released within the localized crime scene or even to the broader locality. Such cases call for tactical, or even strategic responses, again as defined in IAEA TECDOC-1313, depending on the extent of the release. The Litvinenko ^{210}Po poisoning case (33-34), for example, while not, strictly speaking, a nuclear forensic case, nevertheless presented a situation in which the dispersal of radioactive material presented challenges both for forensics and public health.

The technical response to specific nuclear incidents also requires a graded approach. **Categorization** is the analysis performed to understand and address the threat posed by a specific incident, identifying the risk to the safety of first responders, law enforcement personnel, or the public, and determining whether there is criminal activity or a threat to national security. **Characterization**, on the other hand, is a more thorough analysis of the material, performed to determine the nature of the radioactive and associated evidence. **Nuclear forensic interpretation** is the process of drawing validated technical conclusions from the analytical results and correlating the characteristics of the material with material production history. While nuclear forensic interpretation is the end product for the nuclear forensic laboratory, it is an input into the nuclear attribution process. **Full nuclear forensic analysis** includes characterization of all materials, traditional forensic analysis, and nuclear forensic interpretation.

The IAEA report "Nuclear Forensics Support," Nuclear Security Series Number 2, documents a model action plan developed by the ITWG for use in designing a country's response to nuclear trafficking incidents.

Table 1. Selected interdictions of nuclear material around the world

Year	Location	Country	Type	Enrichment/ Pu-239 Content	Mass	Interdiction
1978	New Mexico	USA	NU	0.72%	1500 kg	Theft/Police Investigation
1992	Augsburg	Germany	LEU	2.5%	1.1 kg	Police Investigation
1992	Podolsk	Russia	HEU	90%	1.5 kg	Theft/Police Investigation
1993	Vilnius	Lithuania	HEU	50%	100 g	Police Investigation/Discovery
1993	Andreeva Guba	Russia	HEU	36%	1.8 kg	Theft/Police Investigation
1993	Murmansk	Russia	HEU	20%	4.5 kg	Theft/Police Investigation
1994	St. Petersburg	Russia	HEU	90%	3.05 kg	Theft/Police Investigation
1994	Tengen	Germany	Pu	99.75%	6 g	Police Investigation/Discovery
1994	Landshut	Germany	HEU	87.8%	0.8 g	Police Sting Operation
1994	Munich	Germany	Pu HEU	1.6% 87%	363 g 120 g	Police Sting Operation
1994	Prague	Czech Republic	HEU	87.8%	2.7 kg	Police Operation/Tip-off
1995	Prague	Czech Republic	HEU	87.8%	0.415 g	Police Operation/Tip-off
1995	Prague	Ceske Budejovice	HEU	87.8%	17 g	Police Operation/Tip-off
1995	Moscow	Russia	HEU	20%	1.7 kg	Theft/Police Investigation
1999	Ruse	Bulgaria	HEU	72%	4 g	Border Guards
2001	Paris	France	HEU	72%	0.5 g	Police Operation/Tip-off
2003	Ignalina	Lithuania	LEU	2.0%	60 g	Theft/Police Investigation
2003	Georgia/Armenia Border	Georgia	HEU		170 g	Border Guards/Radiation Detection?
2003	Rotterdam	Netherlands	NU	0.72%	3 kg	Scrap metal
2006	Tbilisi	Georgia	HEU	~90 %	80 g	Police Sting Operation
2007	Pribenik-Lacacseke Border	Slovakia	NU	0.72%	426.5 g	Police Operation/Tip-off
2010	Tbilisi	Georgia	HEU	>70%	18 g	Police Sting Operation

NU- Natural Uranium; LEU- Low Enriched Uranium; HEU- Highly Enriched Uranium

National Objectives

Although the techniques of nuclear forensics are sometimes used in unique applications such as "nuclear archaeology" (4, 35), a term used to describe the analysis and interpretation of nuclear samples of historical interest, the primary purpose of nuclear forensics is to support national objectives. As a relatively new field, many countries are struggling to understand nuclear forensics and define its role in meeting their national objectives. This is made all the more difficult, because nuclear forensics supports two distinct sets of customers, those in law enforcement, who are interested in detecting, capturing, and prosecuting criminals, and those in national intelligence, who are interested in fully understanding the nuclear threat space.

Law enforcement, and subsequent prosecution, requires scientific evidence to support prosecution of nuclear smuggling cases. The evidence presented in court is likely to be the simplest properties of the material, properties that prove that the seized material is illegal, such as elemental or chemical identity, mass, and enrichment level, but these scientific results, and the laboratory system that produced them, must meet all of the national standards for admissibility of evidence (36-37). The requirements of national intelligence, on the other hand, are less well-defined. Law enforcement intelligence is interested in understanding smuggling networks and pathways, so that law enforcement entities can prevent crime, if possible, and detect and punish it, if not. Nuclear intelligence is interested in the state of nuclear capabilities of other countries or non-state actors, such as terrorist groups. Both law enforcement intelligence and nuclear intelligence have broad areas of interest, and are therefore

interested in learning as much about the material as possible. Frequently, these wide-ranging intelligence requirements are framed as a set of questions:

- What is the threat posed by the material?
- Where did the material come from?
- Where did loss of legitimate control occur?
- What were the pathways of the material from loss of control to interdiction?
- Is there more material at large?

The overarching goal of nuclear forensics, then, should be to obtain scientific results that impact on the law enforcement and national intelligence requirements and to convey those results, and their technical interpretation, in a way that makes their meaning clear to those communities. Inherent in this presentation is the concept of "uncertainty." The calculation of the uncertainty for specific analytical results is fairly well understood in theory, if difficult to implement perfectly in practice (38-40). However, the uncertainty of technical conclusions, based upon perhaps dozens of scientific measurements, is less readily apparent. In addition, conveying these uncertainty measurements to policy makers, who typically have non-technical backgrounds and who might have to make decisions of great import using these conclusions, is extremely difficult.

The remainder of this chapter will describe how the various aspects of nuclear forensics work together to support these national objectives of law enforcement and national intelligence (see Figure 2).
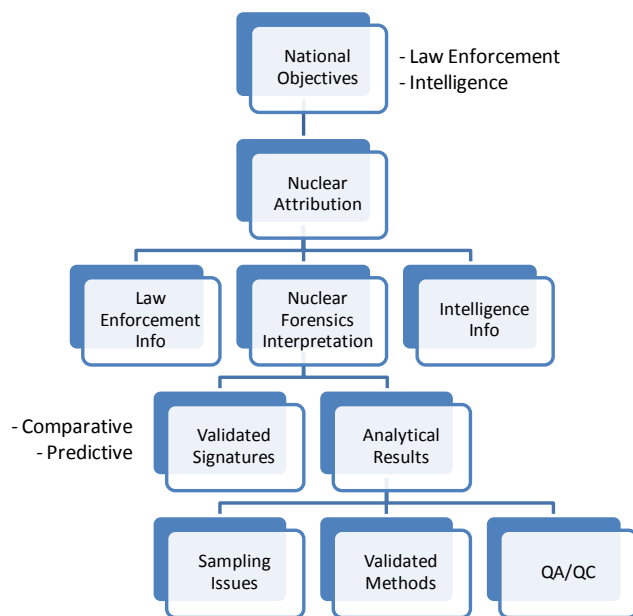

Figure 2
Flow Chart of Attribution Process

Nuclear Attribution

Over the past decade, the nuclear forensics community has distinguished between the terms "nuclear forensics," which is strictly technical in nature, and "nuclear attribution," which is

> *a process to identify the source of nuclear or other radioactive materials used in illegal activities, determine the point-of-origin and routes of transit involving such material, and ultimately contribute to the prosecution of those responsible. . . . Nuclear attribution is the integration of all relevant forms of information about a nuclear smuggling incident into data that can be readily analyzed and interpreted to form the basis of a confident response to the incident. The goal of the attribution process is to answer policy makers' needs, requirements, and questions in their framework for a given incident. (13)*

"Nuclear forensics," as defined, should focus solely on "intrinsic" information, that is, on results obtained from the analysis of the interdicted material and on validated technical conclusions (nuclear forensic interpretation) based upon those results. "Nuclear attribution," on the other hand, utilizes the information provided by nuclear forensics, but also incorporates "extrinsic" information -- from law enforcement, intelligence, and so on. Nuclear attribution, along with some expression of uncertainty in that attribution, is quite likely to be the finished product delivered to national decision makers.

One of the primary goals of the separation of the processes of nuclear forensics and nuclear attribution is the insulation of the nuclear forensic scientist from any biases in their work that might be introduced through knowledge of the extrinsic information. At the same time, though, it is absolutely necessary that those responsible for nuclear attribution, typically senior leaders in the government, have ready access to nuclear forensic experts, so that they can fully understand the implications and limitations of the information provided by nuclear forensics.

Nuclear Forensic Interpretation

Nuclear forensic scientists use the term "signatures" to describe material characteristics that link samples to people, places, and processes, and thus provide information about samples relevant to the set of intelligence questions described previously, much as a written signature can be used linked a document to a specific person. Quite simply, then, nuclear forensic interpretation is the evaluation of analytical results from a sample of interest using a set of validated "signatures" so as to provide technical conclusions to decision-makers. In order to generate high-confidence technical conclusions, we need both results generated using validated analytical methods and validated signatures.

Nuclear forensic interpretation is a deductive process (see Figure 3), much like the scientific method itself. At the beginning of the interpretation process, the nuclear forensic expert develops a hypothesis, or set of hypotheses, based upon the initial analytical results. In most cases, these initial results will be consistent with multiple hypotheses, each of which may suggest additional signatures, that either might be, or must be, present if the hypothesis is true. The expert then devises further tests to verify the presence or absence of the signatures. On the one hand, if these tests show that the required signature

is absent, then the nuclear forensic scientist must abandon his hypothesis or adjust it to fit the new results. On the other hand, if the tests show that the signature is present, then either the scientist has come to a unique technical interpretation, the desired result, or must devise additional tests to exclude the other remaining hypotheses. In the ideal case, only a single hypothesis or interpretation will eventually prove consistent with all results.

In general, one cannot rely on a single signature to answer all of the relevant questions in the case. Some signatures, such as those that derive from isotopic analysis, may only provide general clues that serve to place the material in a broad category like SNM or, perhaps narrow the field of potential countries of origin. Other signatures, such as characteristic dimensions or markings, may provide specific clues that identify a specific facility or date of manufacture. In some cases, a result might only provide information useful for nuclear forensic interpretation when combined with other results. In the same way, independent signatures that reach the same conclusion increase the expert's confidence in the technical interpretation, while results that provide different or even conflicting conclusions decrease this confidence. Nevertheless, a result that seems confusing or insignificant at first may become crucial as the case develops.

Sampling
↓
Categorization
↓
→ Hypothesis Building ← **Case Knowledge**
Knowledge Bases
Archived Material
Other Experts
↓
Analysis
(Radioactive Material &
Traditional Forensic)
↓
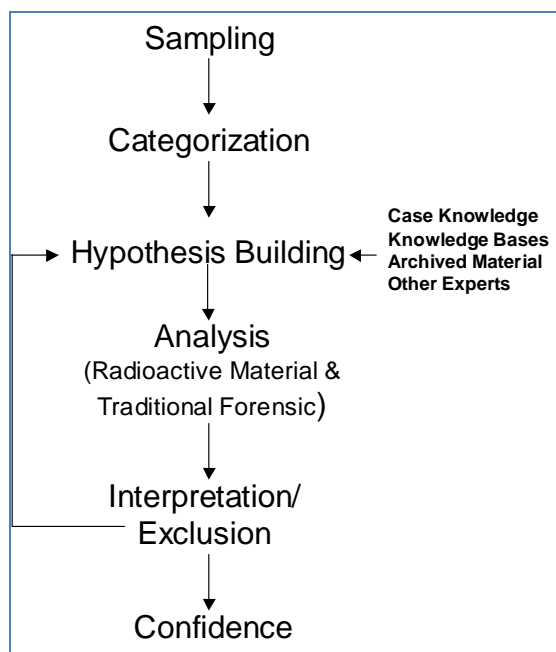Interpretation/
Exclusion
↓
Confidence

Figure 3

Flow Chart of Nuclear Forensic Interpretation Process

Signatures can also work together to increase the specificity of the nuclear forensic interpretation. The outermost box in Figures 4 and 5 represents the universe of potential sources and processes from which the interdicted material may have originated, while the circles demonstrate how a given analytical measurement and associate signature serves to restrict those potential sources and processes. Although increasing the precision of a given measurement could further narrow the field of potential sources or processes that produced the material as shown in Figure 4, it is often more efficient to perform other

types of measurements that employ independent signatures, that is, measurements that verify the presence or absence of signatures different than those of the initial measurement. The confidence in, and the specificity of, the interpretation often increase as more independent measurements are made as shown in Figure 5.
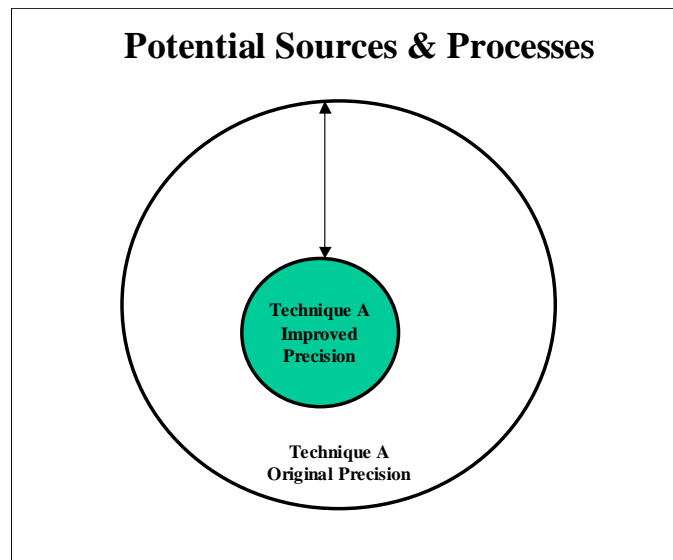
Potential Sources & Processes

Technique A
Improved
Precision

Technique A
Original Precision

Figure 4

The Effect of Improved Precision on Nuclear Forensic Interpretation

Potential Sources & Processes
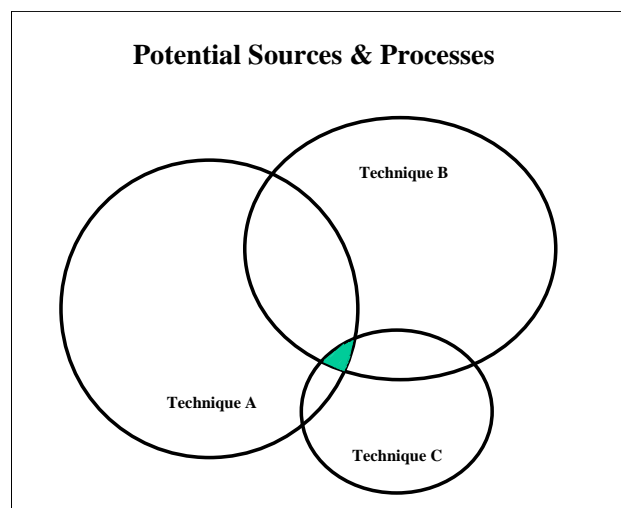
Technique B

Technique A

Technique C

Figure 5

The Effect of Multiple Measurements/Signatures on Nuclear Forensic Interpretation

Validated Signatures

The validation of signatures involves rigorous testing, the extent of the testing depending upon the confidence in the underlying scientific principles that drive the signature, e.g., the principles of radioactive decay in age dating, and the extent to which the signature can be disturbed by factors outside our control, e.g., the nature of the material, the extent and effectiveness of previous processing steps, and the presence of interferences. It is absolutely fundamental that the assumptions that underlie a signature be clearly stated. As far as possible, the nuclear forensic scientist must verify the correctness of those assumptions for the case at hand and, for those cases, where the assumptions cannot be verified, frame the conclusions or adjust the uncertainties to reflect this lack of verification.

Signatures generally fall into two broad categories: comparative signatures and predictive signatures. Comparative signatures involve the comparison of an unknown (or "questioned sample" in law enforcement parlance) to one or more known samples, the essential question being whether the unknown sample is the same as, or similar to, one or more of the known samples. Predictive signatures, on the other hand, involve only an unknown sample, without reference to any known sample or database. Predictive signatures typically derive from underlying physical principles, such as isotopic depletion and activation, in the case of nuclear reactor modeling used to understand the isotopic composition of irradiated material, or radioactive decay in the case of age dating.

Comparative Signatures

Comparative signatures rely on the comparison of an unknown sample with one or more known samples. Nuclear forensic databases, which may contain information on hundreds or thousands of samples, or nuclear forensic sample archives, which may contain tens or hundreds of physical samples, are the natural extension of more targeted sets of known samples. Clearly, the value of this database oriented approach depends on both the relevance and comprehensiveness of the database. In the most general case, the most valuable database for nuclear forensics would include a comprehensive set of material characteristics from materials across the fuel cycle and across the globe. There has already been much discussion in the public policy literature about the importance of international nuclear forensics databases, whether such databases are shared generally or closely held by each country (5, 9, 41).

The importance of these international nuclear forensic databases underscores the importance of international engagement in nuclear forensics. It is important to encourage all countries to develop their own nuclear forensic databases, whether they choose to keep them closely held or not. It is also important that all countries have high confidence in each other's databases, confidence that those databases contain the right materials characteristics for nuclear forensic purposes and that the analytical results contained therein are of high quality. If an interdicted sample is analyzed in France, for example, and compared against a database with analytical results from Russia, there must be strong assurance that both laboratories are providing equivalent results, i. e., that they would get the same answer (within the constraints of analytical uncertainty) when analyzing the same sample. Therefore, international scientific engagement in nuclear forensics, whether conducted in a multilateral setting,

such as through the ITWG, or in a bilateral, country-to-country setting, should drive the standardization of methods, techniques, standards, and reference materials. International exercises or round-robins are absolutely crucial for developing and testing the comparability of nuclear forensic data acquired by different countries.

Although the development of well-populated databases is a necessary step towards discovering and implementing valid comparative signatures, it is equally important to develop validated methods for performing the comparison of analytical results on unknown samples, which may consist of dozens of distinct analytical measurements, each with their own uncertainty, against these well populated databases, which might have information on thousands of materials each with a similar number of measured properties. Currently, our ability to analyze interdicted samples and produce an extensive list of precise materials characteristics far exceeds our ability to interpret the results. Therefore, as we seek to develop the extensive databases necessary for nuclear forensics, we must also develop the comparative methods necessary to produce the necessary inferences from comparison of our analytical results with these large, multidimensional sets of data.

Robel et al. (42-43) tested several multidimensional statistical techniques for comparative analysis against a data set consisting of 50 materials characteristics (mostly concentrations of trace impurities and uranium isotopic composition) measured for approximately 1800 samples of uranium ore concentrate (UOC, sometimes called "yellowcake") from 21 known locations or sources. They found that principal component analysis (PCA) was useful for initially understanding how results from a single source grouped together and how results from different sources related to one another. However, partial least squares discriminant analysis (PLS-DA) was inherently more suited to differentiating between different sources, because PLS-DA uses the source information in constructing its data model (44). However, even a single pass of PLS-DA was insufficient for discriminating between all of the sources in the database. Therefore, they developed an iterative PLS-DA procedure that proved especially adept at identifying the production location of unknown UOC samples. By removing sources which fell far outside the decision boundary of the initial PLS-DA model, and then rebuilding the model, they have consistently produced better and more definitive attributions than with a single pass classification approach.
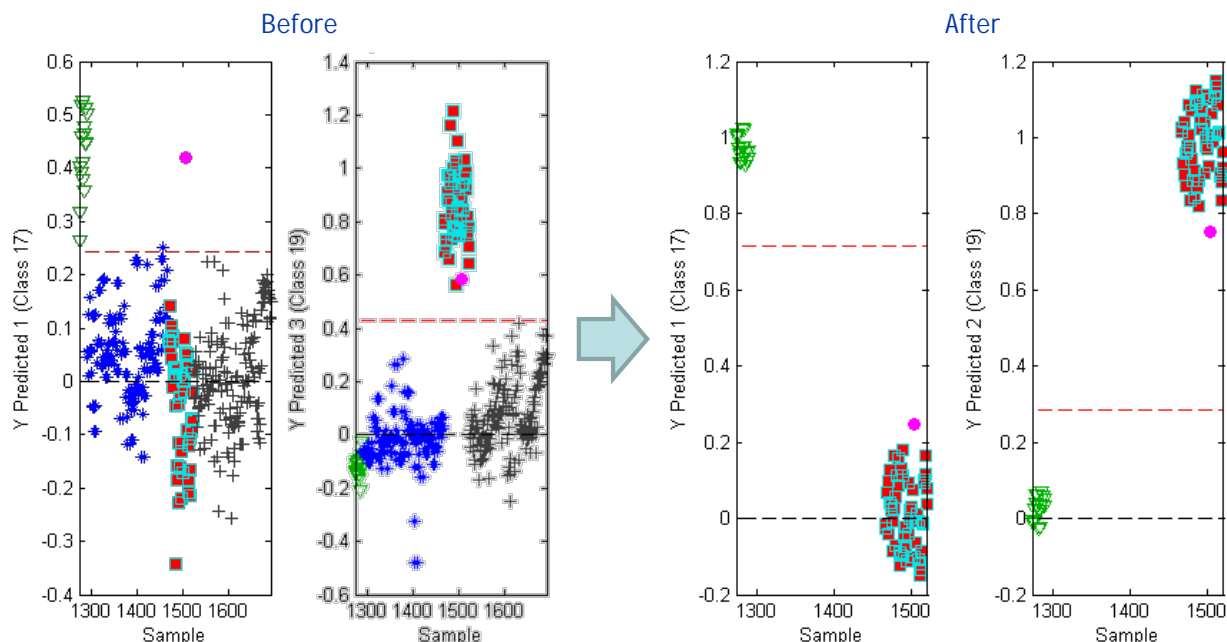
Figure 6

Each data point represents the analysis of an individual sample of material from a given Class (source of uranium ore concentrate). Each Class is represented by a unique symbol. The dashed line is the PLS-DA decision boundary for discriminating between the selected Class and all other Classes in the database. The figures on the left show that an unknown sample (represented by a circular dot) is indistinguishable from material from either Class 17 (triangle) or Class 19 (square). The unknown is distinguishable from Class 18 (star) and Class 20 (cross) (models not shown). After removing Class 18 and 20 from the database and regenerating the PLS-DA models, the figures on the right clearly and correctly demonstrate that the unknown is from Class 19.

Internal validation of the iterative PLS-DA model, in which data from a sample are removed from the comparison database and treated as the analytical data from the unknown (also called "hold one out" validation), achieved 91% accuracy in identifying the source of the UOC. In most cases, the inaccurate predictions chose the right country, but the wrong location within the country. External validation of the iterative PLS-DA model, in which separate physical samples from known locations were analyzed as unknowns, achieved 65% accuracy in predicting the correct source and 90% accuracy in predicting the right country. Furthermore, the iterative PLS-DA method performed better than the classification and regression tree (CART) and k nearest neighbor (KNN) algorithms, with the best combination of accuracy and robustness, for this UOC data set.

For any comparative method, though, it is important to provide some valid estimate of the confidence of its predictions. Internal and external validation exercise, like those described earlier, help one understand the overall reliability of the model. However, only preliminary work on calculating nuclear forensic probabilities or confidence levels for specific predictions has been reported (45). It is also important to understand how specific comparative methods behave when the true source of the unknown sample is not in the database. The iterative PLS-DA approach, for example, always returns a prediction, whether or not the true source can be found in the database. However, statistical

parameters (Q and T_2) generated during application of the iterative PLS-DA approach do provide strong evidence when the ultimate prediction does not fit well with the final model.

Predictive Signatures

With predictive signatures, we seek to calculate identifying material characteristics based on a detailed understanding of the physical or chemical mechanisms responsible for producing the signatures, and adequately modeling those mechanisms to predict the material signatures at a level of specificity required to provide information relevant to the national intelligence questions posed previously. The advantage of the predictive approach is that the processes (and possibly locations) of previously unanalyzed nuclear materials can be inferred from their measured characteristics, something of critical importance for types of materials that are not readily available, e.g., materials from historical processes or tightly-held materials from foreign countries. The disadvantage of the predictive approach is that significant effort must be expended to develop and validate the capability.

Predictive signatures rely, in a general sense, upon our base of knowledge and upon scientific inference, that is, how we apply our existing knowledge to the case at hand. Very little work has been done in building a nuclear forensics-specific base of knowledge, rather, nuclear forensics has been built primarily on other bases of knowledge that already exist. For example, nuclear forensics on materials found early in the fuel cycle, e.g., uranium ores and ore concentrates, relies heavily on geochemistry, a field that studies the chemical and physical processes that govern the composition of rocks, water, and soils both on the Earth and in the universe as a whole. Nuclear forensics of materials found later in the nuclear fuel or found only in the weapons cycle relies upon bases of knowledge developed by various companies as part of their role in the commercial nuclear fuel cycle and by the U.S. and other countries as part of their nuclear weapons programs.

The predictive approach to identifying the source of unknown samples of UOC, for example, involves interpreting signatures measured in a sample of interest to determine characteristics associated with both the parent ore and the mining and milling processes used to produce the UOC from the ore. The predictive approach is more challenging than the comparative approach since it requires a scientific basis for interpreting signatures. Fortunately, many of the chemical and physical processes that created the ore body, as well as the ore concentrate, are well understood through research in geochemistry and economic geology that can be used to develop predictive signatures. For example, the relative concentrations of the rare earth elements (REE) can be typical of the type of ore body from which the uranium was mined (46). The uranium-lead radiometric dating system can be used to determine the age of a parent uranium ore body [47-48]. The samarium-neodymium and rubidium-strontium dating methods can be similarly employed and can also provide indication of the mineralogy of the parent uranium ore [48]. The well-established latitudinal variation of ^{18}O in meteoric water [49-50] influences the ^{18}O isotopic abundance UOC and may provide geographic information.
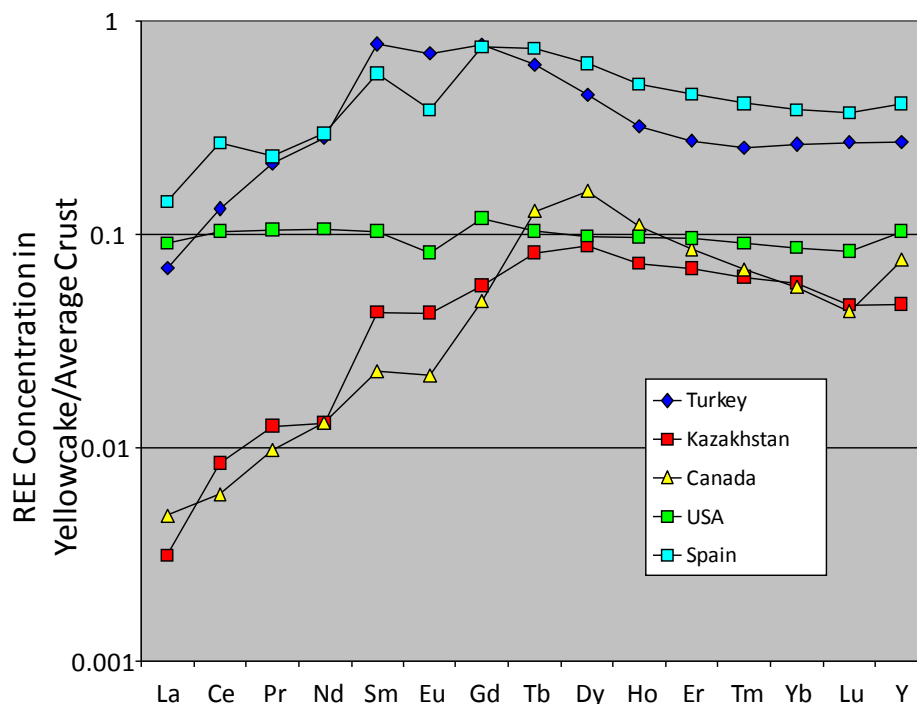
Figure 7

Different ore bodies contain different amounts of rare earth elements. This plot shows the concentration of rare earth elements (relative to the concentrations of the same elements in the earth's crust) for uranium ore concentrate samples from different locations. Reference 42 has shown that the shapes of these REE curves are typical for certain types of uranium deposits.

New predictive signatures are also being developed by establishing improved understanding of the factors that influence distribution of the isotopes of uranium. For example, the fractionation of $^{234}U/^{238}U$ through natural processes has been demonstrated to be indicative of the geological context of an ore [51]. Ores that have been leached by groundwater for long periods of time exhibit a significant depletion in $^{234}U/^{238}U$, whereas ores formed from deposition of those water leachates exhibit a significant enrichment in $^{234}U/^{238}U$. Modern mass spectrometry now provides results of sufficient precision that even natural variations in the $^{238}U/^{235}U$ ratio, once thought to be invariant in nature, can now be investigated. The depositional environment of an ore appears to strongly influence the $^{238}U/^{235}U$ ratio with low-temperature ores having higher ratios than deposits formed at high temperatures [52]. Both of these features of the isotopic distribution of natural uranium are useful signatures for attribution of UOC.

As with all scientific work, it is extremely important to understand, and clearly state, all underlying assumptions when applying predictive signatures, since the validity of the nuclear forensic interpretation will always depend on the validity of those. For example, one of the most frequently applied predictive signatures in nuclear forensics is that of radiochronometry, the determination of the time since last purification using the laws of radioactive decay, a technique commonly known as "age dating." Accurate age dating relies on several assumptions. First of all, there must be a purification

event that quantitatively removes daughter (product) nuclide from the parent (precursor) nuclide. Incomplete purification leads to calculated ages (model ages) that are older than the true time since purification. Second, the sample must remain a closed system from purification until sampling and analysis, precluding both contamination from outside the system and internal segregation of either daughter or parent.

AGE DATING

The principles behind age dating were enumerated in 1905 by Ernest Rutherford. Age dating is a standard tool for disciplines such as geochemistry and cosmochemistry and the use of multiple chronometers is a fundamental precept of these disciplines. In this context, agreement between chronometers indicates a simple (ideal or undisturbed) geologic history, while disagreement indicates a sample has experienced a multi-stage history. (53)

In most case, nuclear forensic samples will not arrive at the laboratory with extrinsic information indicating how well these assumptions hold true for the particular sample. Therefore, it is incumbent on the analyst to test the validity of these assumptions as completely as possible. One of the best ways of doing this is to use multiple chronometers (chronometers based on different parent-daughter radionuclide pairs). If the ages given by the different chronometers "agree" with each other (concordant ages), then we have high confidence that the assumptions for accurate age dating have held true and that the model ages are, in fact, the true ages since purification.

If the chronometers do not agree with each other (discordant ages), then, at a minimum, we must be cautious in the way that the model age dates are interpreted. However, even in such cases, the results from the multiple chronometers can provide valuable information. For example, in the case of the HEU uranium oxide powder seized in Bulgaria in 1999 (24-25), the fact that two chronometers based on trivalent species gave ages slightly, but systematically, older than other chronometers pointed to the use of the Purex process, which is very good at removing some elements (thus re-setting those chronometers completely) and not as good at removing other elements, such as trivalent species, (thus leading to anomalously older ages for chronometers based upon the decay of those species). This inference was possible only due to the use of multiple chronometers.

The analysis of multiple chronometers in LLNL's analysis of samples from the third ITWG round robin (54-57) yielded highly discordant model ages and signaled to the analysts that caution was necessary in interpreting these ages. However, these discordant ages helped focus their attention on the complexities engendered by the uranium casting process (58-61). Participating laboratories were each given two samples of HEU metal (5-6 grams each – see Figure 8). As part of its analysis, LLNL performed age dating using the $^{234}U/^{230}Th$, $^{235}U/^{231}Pa$, and $^{241}Pu/^{241}Am$ chronometers (see Table 2).
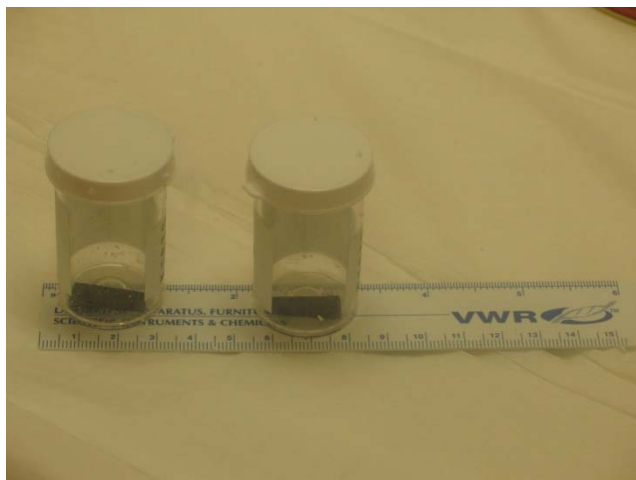
Figure 8

ITWG Round Robin 3 samples (trapezoidal pins of HEU metal) as
received. Reproduced from (54).

Table 2. Model ages calculated from both mass spectrometry
and alpha spectrometry (54).

Measurement	Sample	Units	Mass Spectrometry	Alpha Spectrometry	Years since casting
^{234}U-^{230}Th Age	A	Years	6.894(41)	7.02(67)	6.10
	B	Years	6.074(36)	5.62(65)	6.82
^{235}U-^{231}Pa Age	A	Years	33.73(36)		
	B	Years	35.77(37)		
^{241}Pu-^{241}Am Age	A	Years	14.36(33)	12.3(1.3)	
	B	Years	17.47(37)	15.3(1.9)	

There are two striking features in these results. First, the model age calculated from the ^{234}U-^{230}Th
system corresponds closely to the time since casting (which was only revealed to the participants after
the exercise). Second, there is a total lack of agreement between any of the 3 model ages. The high
concentration of carbon (~0.1-0.2 weight %) found in the samples and the presence of Zr and Er
impurities,which are often used as graphite mold coatings, suggested that the uranium in each of the
samples had been recast multiple times. It was therefore clear that the casting process must have
caused a segregation of the Th in the material, such that Th was completely removed from the center of
the initial casting (where the round robin samples were taken). However, this process did not result in
the complete removal of other impurities, such as Pu, Am, or Pa. The segregation of radioactive
impurities into the top of uranium castings (the so-called "hot top"), especially in the presence of high
concentrations of carbon, has been observed for some time (57-58), so it appears that, while Th was
completely removed from the center of the casting by this process, the other species were either
removed partially or not at all.

Without extrinsic knowledge of the sample, though, we have to be very careful in interpreting model ages. For instance, we did not know *a priori* anything about the casting shape (other than what we deduced from the shape of the solid pieces themselves) or the method of sampling. These could have very well have been from the "hot top," for example, and resulted in the determination of an anamolously old model age. Even now, with knowledge of the casting shape and process, we still don't know how generalizable this result is. We still lack the fundamental studies necessary to extrapolate this single point measurement to the more general case where the conditions of casting might be expected to vary widely (with unknown effects on impurity segregation).

In summary, then, the measurement of multiple chronometers in nuclear forensics is critical for testing whether the fundamental assumptions of age dating have held true for the sample in question. If we obtain agreement between model ages from different systems, we can posit that age as the true time since purification more confidently, since the likelihood that two or more chemical systems will be contaminated or fractionate in precisely the same way is very low. On the other hand, if we obtain disagreement between model ages from multiple systems, then we know to exercise caution when interpreting those ages. In fact, such systematic variations in the ages can often provide insight into the chemical and physical processes used in preparing the material.

Although the uncertainty regarding one's assumptions clearly affects the uncertainty of the state conclusion, measuring that uncertainty in an unbiased way and then incorporating that uncertainty into the overall uncertainty of the conclusion is not straightforward and remains work to be done.

Analytical Results

Nuclear forensics is not amenable to a "cook book" approach that can be universally applied to all evidence, but, rather, involves an iterative approach, in which the results from one analysis are used to guide selection of subsequent analyses. However, the nuclear forensics community has defined 3 levels of analysis, categorization, characterization, and full nuclear forensic analysis, each of which serves a unique purpose in the investigation as described below. In all cases, though, laboratory sampling and analysis must be performed with due regard for preservation of evidence and perpetuation of chain-of-custody, since many of the analytical tools used in these analyses are destructive, that is, they consume some amount of sample during analysis. Therefore, the proper selection and sequencing of analyses is critical.

Categorization

On-site non-destructive analysis (NDA) using field-portable gamma-ray spectrometry or X-ray fluorescence aims to categorize the suspected radioactive material without affecting the evidence. The goal of categorization is to identify the bulk constituents of the material in order to assess the threat posed by the material and confirm whether the seized evidence is contraband, something which would form the basis for continued investigation. Such non-destructive analyses can quickly distinguish between naturally occurring radioactive material, special nuclear material, radioactively contaminated material, or a commercial radioactive source.

Further analysis will be guided by this initial categorization. The next analyses to be performed will be based upon the ultimate goals of the investigation (basic characterization versus full nuclear forensics analysis – see below), the information uncovered so far, the potential signatures (physical, chemical, elemental, isotopic) that might lead to precise interpretation, the amount of sample available for analysis, and methods for measuring forensic signatures.

Characterization

Characterization aims to determine the nature of the radioactive evidence and provide detailed results for officials to make informed decisions. Characterization of the radioactive material includes complete elemental analysis, including major, minor, and trace constituents, as well as isotopic and chemical phase information for all major constituents. Characterization also includes physical characterization, including accurate measurement of the critical dimensions of solid samples, determination of particle size and shape distributions for powder samples, and high magnification imaging of the material by optical and scanning electron microscopy. Characterization does not include analysis of traditional forensic signatures nor detailed nuclear forensic interpretation (identification of candidate source locations and processes, for example). Characterization will take more time than categorization, but less time than the full nuclear forensics analysis, approximately 1 to 4 weeks after receipt of the samples.

Full nuclear forensics analysis

The goal of full nuclear forensics analysis is to analyze all radioactive and traditional forensic evidence in order to provide information for answering the questions of both law enforcement and intelligence, including identifying the material's origin, method of production, means by which legitimate control was lost, transit routes from diversion to interdiction, and probability that more material exists. Full nuclear forensics analysis would include detailed nuclear forensic interpretation and might include predictive techniques such as reactor modeling and comparison against nuclear forensics databases or sample archives, so as to identify the method of manufacture and probable sources of the material. Full nuclear forensic analysis will take the longest amount of time, up to two months after receipt of the samples.

Validated Methods

Some analytical methods provide strictly qualitative information, e.g., color, shape, identifying markings, but most analytical methods are quantitative, providing mean values and associated uncertainties for various characteristics of the material, e.g, mass, dimensions, trace elemental composition. These means and uncertainties allow the application of the validated signatures to the material at hand. The analytical techniques described in the following sections are commonly used in nuclear forensic analysis. However, it is important that specific methods used to generate nuclear forensic results, either by these or other methods, be validated to ensure high quality technical conclusions.

The validation of analytical methods involves rigorous testing to ensure that the strengths and limitations of the method are well characterized and that the results generated are fit for the intended purpose. In particular, characteristics of the technique, such as specificity, sensitivity, precision, and accuracy should be determined and documented. Specificity refers to the ability of the technique to measure the analyte of interest in the presence of all other constituents in the sample. The presence of

interferences, for example, will degrade the specificity of any technique. <u>Sensitivity</u> refers to the change in analytical signal with the amount of analyte present. If one combines the concept of sensitivity with the concept of "background," the amount of analytical signal present in the absence of analyte, one derives the detection limit of the technique, that is, the smallest amount of analyte that can be detected at some specified confidence level. <u>Precision</u> usually refers to the variation in the analytical signal (or the quantity of analyte calculate from that signal) over time, with repeated measurements. When combined with other sources of uncertainty in the measurement, e.g., uncertainties in the knowledge of dead time or uncertainty in the calibration standards, one can calculate the "combined uncertainty" of the measurement. <u>Accuracy</u>, of course, refers to how closely our reported results match the true value.

For an unknown sample, the true value is not known, so we rely on validation of the method and ongoing performance testing for estimates of the accuracy of the technique. The method is typically validated through the analysis of known samples, such as certified reference materials (CRM) from national or international standards laboratories or other standards with values traceable to those CRMs. However, appropriate certified reference materials or traceable standards are not available in all cases, necessitating the use of self-prepared standards or other well characterized samples. We always seek to achieve accuracy within the stated uncertainty of our measurement. If we have a consistent bias (inaccuracy) in our reported results and this bias cannot be eliminated, by recalibration, for example, then we include this bias in the calculation of uncertainty. It is worth noting that these underlying uncertainties in the analytical measurement will eventually propagate through to the uncertainty in the nuclear forensic interpretation, combining with uncertainties in the signatures, and so forth.

Radioactive Material Analysis

The nuclear forensic scientist has a wide array of analytical tools to use for detecting signatures in radioactive material. These individual techniques can be sorted into three broad categories: bulk analysis tools, imaging tools, and microanalysis tools.

<u>Elemental and Isotopic Bulk Analysis Tools</u>

Bulk analysis tools allow the forensic scientist to characterize the elemental and isotopic composition of the radioactive material as a whole. In some cases, bulk analysis is necessary to have sufficient material to adequately detect and quantify trace constituents, which are often vitally important as signatures for certain manufacturing processes, for determining the time since chemical separation (age dating), and for determining whether the material has been exposed to a neutron flux.

Radiometric Techniques
Each radioactive nuclide emits radiation of known types and energies at rates determined by the quantity present and its characteristic half-life (or decay constant). Therefore, by measurement of the type and intensity of radiation emitted from a sample, it is possible to quantify the amount of each radioactive nuclide present. There are three types of radiation that are commonly considered for measurement, alpha, beta and gamma radiation, each with its own properties and methods of detection. Alpha radiation is commonly detected by silicon surface barrier detectors, beta radiation by

scintillation techniques or gas ionization detectors, and gamma radiation by high purity germanium crystals.

Gamma spectrometry has a dual role in nuclear forensics. For on-site applications high-resolution gamma spectrometry is mostly used only to quickly identify the material and obtain a rough idea about the isotopic composition of the material, i.e., categorization. If a radiation source or radiological dispersal device (RDD) is detected, gamma spectrometry can be deployed on the spot in order to identify the radioactive isotopes present (which are not necessarily nuclear), without dismantling the source or device. In the laboratory, high-resolution gamma spectrometry is used to provide an initial determination of the isotopic composition of uranium and/or plutonium, as well as detection and quantification of trace fission and activation products in the sample, e.g., in uranium from reprocessed reactor fuel.

Alpha spectrometry is used to quantify the abundance of alpha-emitting radionuclides, particularly those with relatively short half-lives. Because source preparation is crucial for achieving good energy resolution in alpha spectrometry, the target elements are usually separated and purified before deposition onto a flat surface. Quantification is achieved by spiking the samples with known amounts of an isotopic spike or tracer. Alpha spectrometry is especially suited for quantifying ^{232}U and ^{238}Pu due their short half-lives and, in the case of ^{238}Pu, the potential interference from ^{238}U in mass spectrometry. However, alpha spectrometry is not able to separate the peaks due to ^{239}Pu from ^{240}Pu, nor is it sensitive to ^{236}U. Therefore, full characterization of the isotopic composition of Pu and U must include both alpha spectrometry and mass spectrometric analysis. Alpha spectrometry may also be used to quantify ^{241}Am (daughter of ^{241}Pu), which can then be used to calculate the date of the last plutonium purification performed on a sample (assuming complete purification), and ^{230}Th (daughter of ^{234}U), which can similarly be used to determine a last purification date for uranium materials.

Because beta particles are emitted with a broad range of energies, beta spectrometry must be combined with chemical separation and purification of the target element in order to quantify a specific nuclide. In some cases, nuclides emit a gamma ray simultaneous with the emission of a beta particle; a combined beta-gamma measurement can provide additional specificity for the analysis.

Mass Spectrometry

Mass spectrometry is used to determine both the elemental and isotopic composition of nuclear materials, offering extremely high precision and accuracy of analysis and the capability to determine both radioactive and stable isotopes. In mass spectrometry, atoms or molecules are converted into positively or negatively charged ions, which are then separated according to their mass-to-charge ratio and the intensities of the resulting mass-separated ion beams measured. Mass spectrometry can provide quantification (often called an "assay" when applied to major constituents of the sample) of elements either by using an isotopic spike (isotopic dilution mass spectrometry) or through calibration against standard solutions in the case of solution-based techniques like inductively coupled plasma mass spectrometry.

Thermal Ionization Mass Spectrometry

In Thermal Ionization Mass Spectrometry, (TIMS), a sample is deposited on a metal filament, through which a current is passed to heat it to high temperatures inside the vacuum of the mass spectrometer. If the ionization potential of a given element is low enough compared to the work function of the filament, then a fraction of the atoms of that element are ionized via interaction with the filament surface at high temperature. Specificity of the TIMS analysis can be enhanced both by chemical separation steps and the ionization temperature. TIMS is capable of measuring isotopic ratios on picogram (10^{-12} gram) to nanogram (10^{-9} gram) samples or down to tens of femtograms (10^{-15} grams) using special pre-concentration techniques. TIMS routinely measures differences in isotope mass ratios on the order of 1 in 10^6. Multicollector TIMS instruments, instruments with detectors able to measure all multiple isotopes simultaneously, are now available for very precise measurements of isotopic composition. TIMS is the preferred technique for measuring Sr and Nd isotope ratios.

Inductively Coupled Plasma Mass Spectrometry

In Inductively Coupled Plasma Mass Spectrometry, (ICP-MS), the sample is aspirated as a solution into an inductively coupled plasma, where the high temperature of the plasma serves to atomize and ionize the sample with high efficiency. Multicollector ICP-MS instruments (MC-ICP-MS), instruments with detectors able to measure all multiple isotopes simultaneously, provide some of the most precise measurements of U and Pu isotopic composition. In addition to measuring isotopic composition, ICP-MS is useful as a method for precisely quantifying trace elemental constituents of a sample with detection limits ranging from 0.1 parts per billion (ppb) to a few tens of ppb in solution. ICP-MS has difficulty measuring some elements due to background, interferences, or poor ionization efficiency, e.g., C, O, P, K, S, and Si.

Chemical Assay

Chemical titration and coulometry are standard methods for the determination of the elemental concentration of uranium, plutonium, neptunium, and other nuclear materials. In chemical titration, precisely measured amounts of a selective reagent are added to a known mass of sample in solution. The reagent, reacting with the element of interest according to a well known stoichiometric reaction, is added until the element of interest has completely reacted, the "end point." The end point can be detected either via potentiometric (electrical) or spectrophotometric (optical) methods. In controlled potential coulometry the element to be analyzed is selectively oxidized or reduced at a metallic electrode maintained at a suitably selected potential. The number of electrons used in the oxidation or reduction is a measure of the amount of element present in the sample. The precision and accuracy of these two assay methods can be better than 0. 1% and can be very effective for the characterization of interdicted materials, provided that samples of at least a few tenths of a gram are available for this analysis.

Radiochemistry

Many samples are too complex for all the radioactive isotopes present to be measured directly. By utilizing the differences in chemical properties of the elements it is possible to devise schemes of chemical reactions to separate and purify elements, or groups of elements, allowing the measurement of radioactive nuclides of those specific elements by either radiometric methods, or mass spectrometry. The concentration of specific isotopes can be related back to the original sample by referencing to an

internal isotopic standard called a "spike," added during the radiochemical preparation. The chemical separation and purification steps increase both the sensitivity and selectivity of the technique. Radiochemistry is especially important for the measurement of isotopes at low activity levels. Radiochemistry, in combination with radioactive counting techniques or mass spectrometry, has the potential to measure down to 10^6 atoms or lower of certain isotopes.

X-Ray Fluorescence Analysis

X-ray fluorescence (XRF) can also be useful for broad and non-destructive elemental quantification of either solid samples or solutions. An incident X-ray beam excites characteristic secondary X-ray wavelengths and energies in a solid sample that are counted on a solid-state or proportional counter. The detection limits for XRF are generally in the range of 10 ppmw, although actinide matrices generate many X-rays that interfere with the lower-energy X-rays of lighter elements. Using wavelength dispersive analysis of the X-rays (WDS) provides higher energy resolution than energy dispersive analysis (EDS), which can be used to resolve some of these interferences (see X-ray Analysis discussion below). Analysis of light elements is also problematic due to low characteristic x-ray energies and consequently poor detection probabilities.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) is the standard method for identifying the chemical structure of inorganic and organic crystalline materials. X-ray beams that impinge on regularly ordered lattices undergo constructive and destructive interference that depends on the spacing of the lattice, the wavelength of the X-rays, and the angle of incidence of the X-ray beam. By rotating the sample relative to a fixed X-ray source, variations in interference occur, leading to characteristic diffraction patterns. These diffraction patterns can be compared to reference spectra to identify the specific crystalline phase. XRD cannot generate diffraction patterns from amorphous (non-crystalline) materials.
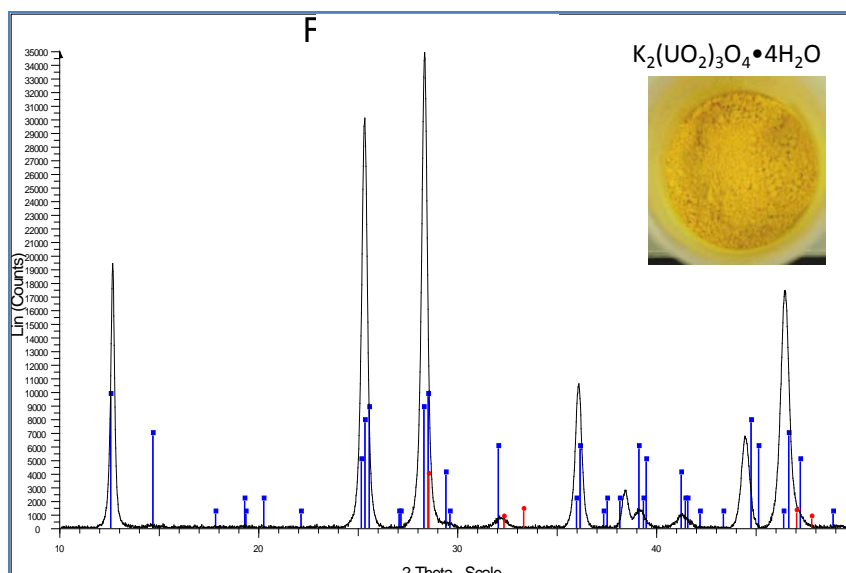
Figure 9

XRD spectrum of interdicted uranium powder (shown in inset), identifying an unusual
potassium-containing compound, related to potassium diuranate. Reproduced from (62).

Gas Chromatography/Mass Spectrometry

Gas chromatography/mass spectrometry (GC/MS) is a technique useful for detecting and measuring
trace organic constituents in a bulk sample. In GC/MS, the components of a mixture are separated in the
gas chromatograph (GC) and identified in the mass spectrometer. The primary component of a GC is a
narrow bore tube (called a "column"), which is maintained inside an oven. In the simplest arrangement,
the mixture is flash vaporized in the heated introduction port. The various components of the mixture
are swept onto, and through, the column by the carrier gas (usually He). The components of the mixture
are separated on the column based upon their volatility and relative affinity for being on the column
material versus the carrier gas. Columns are usually coated with a special material to enhance
separation of the components of interest. In the ideal case, all components are separated and
introduced into the mass spectrometer one at a time. At low flow rates, the column effluent can be
introduced directly into the mass spectrometer. At higher flow rates, the GC requires an interface to
match the flow requirements of the mass spectrometer, usually by selectively removing the carrier gas.

The mass spectrometer ionizes and fragments each component as it elutes from the column. Many
different ionization methods can be used, but the most common for GC/MS is electron impact (EI). In EI,
an energetic (70 eV) beam of electrons bombards the sample molecules. Some of these electrons will hit
a sample molecule and knock out an electron, leaving the molecule positively charged. This ionizing
collision tends to impart some energy to the molecule. This energy is sometimes great enough to cause
the ion to fragment (usually into an ion and a neutral fragment) in ways characteristic of the molecule's
structure. The relative abundance of ions of various masses (strictly mass-to-charge ratio, although the
typical ion charge in EI is usually 1) is characteristic of the intact molecule. The mass spectrometer

measures the intensity of ions of various masses, either by simultaneous or sequential detection, depending on the type of mass spectrometer. The resulting plot of relative intensity versus mass-to-charge ratio is a "mass spectrum." There are now extensive libraries of EI mass spectra that help identify unknown compounds that are separated and detected by the GC/MS.

Imaging Tools

While bulk analysis provides an integrated compositional measurement of the sample as a whole, and consequently may obscure important signatures in underlying components, imaging tools provide high magnification images or maps of the material that can confirm sample homogeneity or heterogeneity. Imaging techniques are especially important for assessing the morphology and microstructure of the material.

Visual Inspection and Photography
Visual inspection of a sample can often help in identifying the nature of a sample, especially in conjunction with data from the initial categorization. Size and shape can be sufficient to identify some items, especially if serial numbers or other identifying marks can be seen. For chemicals the color and form of the material can be important clues.

Optical Microscopy
Optical microscopy is often the first method to examine the sample at high magnification. An optical microscope uses magnifying light optics and reflected or transmitted methods of sample illumination to present magnified images of the sample to the user's eyes. Viewing samples under polarized light can also reveal information. Light microscopes can readily magnify an image up to x1000.
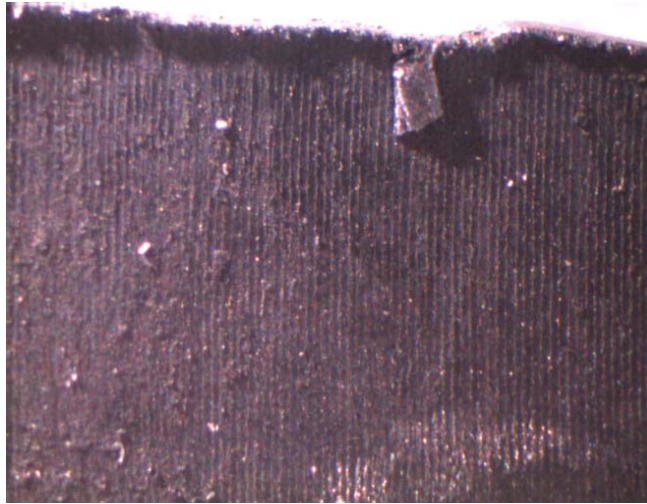
Figure 10

Optical photomicrograph of the surface of one of the ITWG Round Robin 3 samples. The
regular striations (~15/mm) on the surface were caused by slow cutting with a band saw.
The rough cut edge was also cut with the band saw, but at a much faster rate.
Reproduced from (54).

Scanning Electron Microscopy

Scanning electron microscopy (SEM) can provide image magnifications up to x 10 000 with a
conventional thermal filament source or x 500,000 times with a field emission source. In SEM, a finely
focused electron beam is rastered or scanned over the sample. The interaction of the energetic incident
electron beam and the sample produces backscattered electrons, secondary electrons, and X-rays. By
measuring the flux of one of these types of particles as a function of raster or scan position, an image or
map of the sample can be reconstructed and displayed. Each type of particle conveys different
information about the sample and, therefore, offers a different contrast mechanism. For instance,
secondary electrons carry information about sample topology. Backscattered electrons carry
information about average atomic number of the area being imaged and can be used to quickly detect
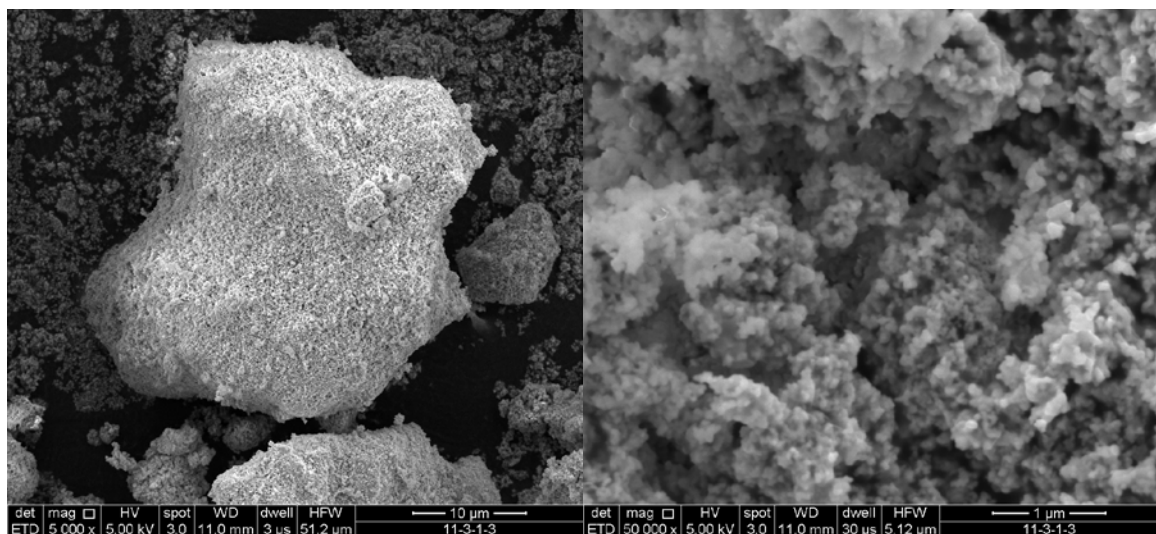spatially resolved phases of contrasting chemical composition.

Figure 11

SEM photomicrographs of the interdicted uranium powder shown in Figure 9. The morphology of the powder was consistent with a hydroxide precipitation process (probably KOH). Reproduced from (62).

Transmission Electron Microscopy

In transmission electron microscopy (TEM), the energetic electron beam is transmitted through an ultra-thin sample (~100 nm thickness). TEM is capable of higher magnifications (several million times) than SEM and is able to image extremely fine structure, but at the expense of tight restrictions on sample thickness. In most cases, thin sections of the sample must be made. Transmitted electrons can undergo diffraction effects, which can be used like XRD to determine crystal phases in the material.
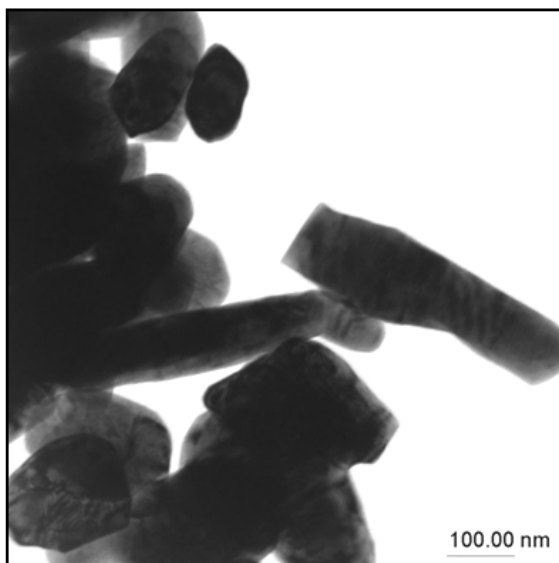

Figure 12

TEM image of the Bulgarian HEU oxide sample, showing two distinct morphologies in the constituent particles. Reproduced from (24).

Microanalysis Tools

If imaging analysis confirms that the sample is heterogeneous, then microanalysis tools can often quantitatively or semi-quantitatively characterize the individual constituents of the bulk material. The category of microanalysis tools also includes surface analysis tools, which can detect trace surface contaminants or measure the composition of thin layers or coatings, either of which could be import for interpretation.

X-Ray Microanalysis
The X-rays generated during SEM or electron microprobe analysis carry elemental information and are a convenient way of measuring the elemental composition of micro-samples or particles. The X-rays can be analyzed by either of two methods. First, an energy dispersive spectrometer (EDS) uses a solid state detector (typically a Si(Li) detector) to measure simultaneously the energy and rate of incident X-rays. Second, a wavelength dispersive spectrometer (WDS) uses a synthetic analyzing crystal to sequentially diffract selected X-rays into a gas proportional counter. Due to the interaction mechanics of the electron beam with the sample, X-rays are generated over approximately a ~1 μm, tear drop-shaped region. Thus, X-ray analysis is limited to spatial resolution of around 1 μm. The detection limits of X-ray analysis are approximately 0.01 - 0.1 %, depending on the element. X-ray microanalysis is an assay technique to measure the elements at greater than 0.01% rather than a trace element analysis technique.

Secondary Ion Mass Spectrometry
Secondary ion mass spectrometry (SIMS) can be used for both elemental surveys and isotopic analysis of small samples, even particles. SIMS uses a finely focused primary ion beam, e.g., O_2^+, Cs^+, or Ga^+, to sputter the sample surface. The sputtering process produces secondary ions (ions characteristic of the sample) that can be analyzed by a mass spectrometer. SIMS is capable of acquiring microscopic images of isotopic distributions (which can correspond to elemental images for known elements of known isotopic abundance). In the "microscope" mode a relatively large primary ion beam bombards the sample, and the spatial position of the resulting secondary ions is maintained and magnified throughout the mass spectrometer. An imaging detector then displays and records the resulting isotopic image. In the "micro beam" mode a finely focused primary ion beam is rastered or scanned across the sample in a manner similar to an electron microscope. The resulting secondary ion signal is then measured and correlated with the position of the primary ion beam to generate the isotope image. Sample ablation of the focused ion beam on the sample yields a depth profile through the sample surface that is extremely valuable to document compositional gradients or surface alteration.
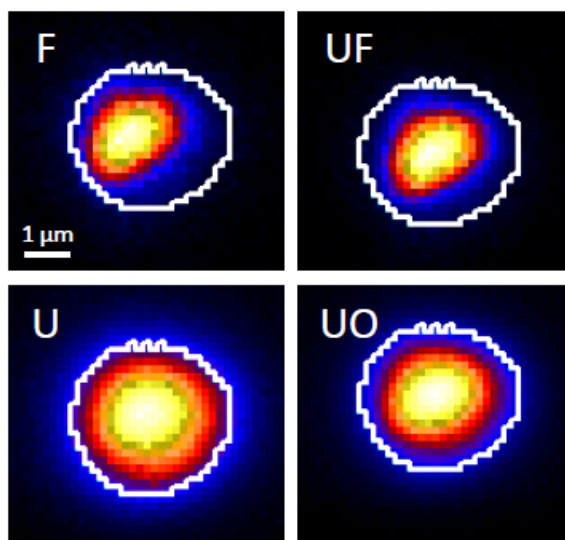
Figure 13

Ion intensity images using the CAMECA NanoSIMS at LLNL. The images are displayed in the false color mode, in which white/yellow corresponds to the highest ion intensity and blue/black to the lowest ion intensity. These images clearly show the the uranium oxyfluoride particle (generated at the European Institute for Reference Materials & Measurements under laboratory conditions) is losing F from the outside of the particle inward. (SIMS conditions: 45 pA O- primary ion beam, 16 keV impact energy.)

Infrared Spectroscopy

Infrared Spectroscopy (IR) is useful for the identification of organic compounds. Through the use of a specialized microscope, IR can be performed on samples as small as 15 μm and is an important microanalytical technique. Molecular bonds vibrate at characteristic frequencies. If a particular molecular vibration results in a change in the bond's dipole moment, then the molecule can absorb infrared radiation of that characteristic frequency, exciting that vibration.

In IR the sample is irradiated with a broad band of infrared frequencies, and the intensity of the reflected or transmitted infrared radiation is measured as a function of frequency. From the knowledge of incident intensity and reflected/transmitted intensity as a function of infrared frequency, an infrared absorbance spectrum can be reconstructed. Absorption at specific frequencies is characteristic of certain bonds. Thus, the IR spectrum identifies the various bonds and functional groups within the molecule. In addition, there are also vast libraries of IR spectra that help identify unknown compounds or, at least, place them into certain classes of molecules.

Raman Spectroscopy

Raman Spectroscopy is also useful for the identification of organic compounds and is complementary to IR, since some molecular vibrations are Raman active and some are infrared active. Through the use of a specialized microscope, Raman spectroscopy can be performed on samples as small as 1 μm. If a

particular molecular vibration results in a change in the polarizability of the molecule, then the molecule can absorb radiation of that characteristic frequency, exciting that vibration.

In Raman the sample is irradiated with radiation of a specific frequency, and the intensity of the reflected radiation is measured as a function of frequency. Most of the radiation is reflected at the same frequency as the incident radiation. However, some radiation is reflected at specific frequencies of lower energy (Stokes lines) and some at specific frequencies of higher energy (anti-Stokes line). The frequency shifts between the Stokes and Anti-Stokes lines and the incident radiation correspond to Raman active vibrations.
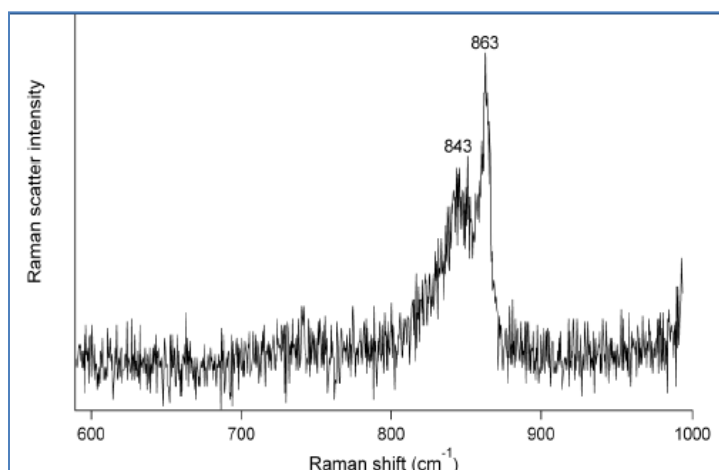

Figure 14

Raman spectrum of uranium oxyfluoride compound. The peak at 863 cm^{-1} is indicative of the uranyl moiety, while the peak at 843 cm^{-1} is indicative of degradation due to further hydration and loss of fluorine over time.

Table 3.
Examples of Analytical Tools for Nuclear Forensics

Measurement Goal	Technique	Type of Information	Typical Detection Limit	Spatial Resolution
Survey	HRGS	Isotopic	ng-µg	
Elemental and Isotopic Bulk Analysis	Chemical Assay	Elemental	mg	
	Radiochemistry / Radiometric Methods	Isotopic, Elemental	fg-pg	
	TIMS	Isotopic Elemental	pg-ng	
	ICPMS	Isotopic Elemental	pg-ng	
	XRF	Elemental	10 ppm	
	XRD	Molecular	~1 at%	
	GC / MS	Molecular	ppm	
Imaging	Visual Inspection	Macroscopic		0.1 mm
	Optical Microscopy	Microscopic		1 µm
	SEM	Structure		1.5 nm
	TEM			0.1 nm
Microanalysis	SIMS	Elemental Isotopic	0.1 ppb-10 ppm	0.2-1µm
	SEM/EDS or WDS	Elemental	0.1-2 wt%	1µm
	FTIR	Molecular	.1-1 wt %	15 µm
	Raman	Molecular	~1 wt %	1µm

Legend:

mg = milligram = 10^{-3} gram   at% = atom percent
µg = microgram = 10^{-6} gram   wt% = weight percent
ng = nanogram = 10^{-9} gram   ppm = parts per million by weight
pg = picogram = 10^{-12} gram   ppb = parts per billion by weight
fg = femtogram = 10^{-15} gram   µm = micrometer = 10^{-6} meter

HRGS= High Resolution Gamma Spectrometry
TIMS= Thermal Ionization Mass Spectrometry
ICPMS= Inductively Coupled Plasma Mass Spectrometry
XRF= X-ray Fluorescence Analysis
XRD= X-ray Diffraction Analysis
GC/MS= Gas Chromatography / Mass Spectrometry
SEM= Scanning Electron Microscopy
TEM= Transmission Electron Microscopy
SIMS= Secondary Ion Mass Spectrometry
SEM/EDS= Scanning Electron Microanalysis with Energy Dispersive Sensor
SEM/WDS= Scanning Electron Microanalysis with Wavelength Dispersive Sensor
FTIR – Fourier Transform InfraRed Spectroscopy

Traditional Forensic Analysis

Overview
Traditional forensic analysis, like radioactive materials analysis, is an iterative process, in which the results from one analysis are used to guide the selection of subsequent analyses. The forensic analyst must carefully examine all of the items seized at the incident site in order to uncover as much information as possible; unlikely, and apparently unrelated, evidence are often the keys to the successful prosecution of a case.

There is a great variety of traditional forensic evidence, as well as methods of collection and evaluation. For example, evidence such as tissue, hair, fingerprints, and shoeprints can often associate a specific individual with a specific place or object. The analysis of fibers, pollen, or chemical substances found at the incident scene can provide information about motives or transportation routes. Documentary evidence provides useful information not only in the content of the communication itself, but also in the incidental details of its creation (paper, ink, film type, extraneous noises, and accents). Therefore, the following list of examples is not exhaustive.

Once again, all sampling and analysis must be performed with due regard for perpetuation of the chain-of-custody and preservation of evidence, since the sampling process itself could contaminate or destroy some evidence in the pursuit of other evidence. In addition, the collection of traditional forensic evidence on radioactively contaminated materials must also be performed in a manner consistent with good radiological safety practice.

Documentary Evidence
Documents or recordings (from an answering machine, for example) can provide information, not only through the written or recorded information itself, but also through other evidence that ties the document or recording to a person or place: detailed analysis of handwriting, type characteristics and anomalies on typed documents, photocopier characteristics and anomalies on photocopied documents, and mechanical impressions for typeset documents. Analysis of the paper used in a document can itself provide valuable clues. The analysis of paper associated with the Bulgarian seizure, for example, indicated a source somewhere in eastern Europe, for example (24). Examination of a recording would include an analysis of the language, dialect, and stray background sounds. If a computer, or a data storage media, e.g. disk, is recovered from the incident scene, then the forensic analyst must try to recover all of the information stored there. Programs and files may document the perpetrators' plans and methods and/or implicate other people. Information stored in mobile phones could also provide useful information.

Impressions
Latent fingerprints, palm prints, or prints from other body areas, e.g. ear prints from listening at windows, could tie a person to a location or an object seized in the incident. Shoe prints discovered at the incident site can also link a specific person to the incident site, through the unique tread pattern of their shoes. Similarly, tire treads could serve to link a specific car to the incident site.

Chemical Analysis

Unique or special chemical substances seized at the incident site can provide valuable evidence. Controlled substances or poisons may provide useful information about the perpetrators or their motives. Accelerants used for arson or explosive residues provide evidence about methods and purpose. Characteristic dyes and petroleum products can tie the seized evidence to particular locations, perhaps serving as a marker for route interpretation.

Tissue and Hair Evidence

Human tissue recovered at the incident scene can also tie a specific individual to the incident scene or seized evidence. Blood can be typed through serology. Blood and other tissue can be subjected to either nuclear or mitochondrial DNA analysis, again helping to implicate an individual. Hair samples can provide information about race and body characteristics.

Weapons Evidence

In the event that a bomb is detonated or seized, the bomb remains and explosive residues can provide a pattern for determining the type of bomb and its method of manufacture. Unique materials may pinpoint the exact perpetrator or, at least, restrict the number of potential perpetrators through purchase records for such material. In the event that firearms are seized, the examination of the projectile lead, cartridge cases, gunshot residues, and any altered function may tie the perpetrator to a given location, a fact useful in route interpretation, or it may provide evidence of method or purpose.

Tool Marks

Alterations in objects that appear to be made by the perpetrators themselves are highly significant. The forensic analyst should look for fractures (particularly those that match up with other fractures in the evidence), odd marks in wood, the use of stamps and dies, and the modification of locks and keys. The forensic analyst should attempt to restore any obliterated markings. For example, the regularly spaced grooves on the ITWG Round Robin 3 samples (see Figure 10) were indicative of cuts made by a slow-moving band saw.

Fiber Examination

Fibers can serve to tie objects and perpetrators to specific locations as well. The forensic analyst must pay particular attention to fiber evidence, such as fabrics, cords, and ropes and determine its type: animal (wool), mineral (glass), synthetic, or organic (cotton).

Flora and Fauna

The forensic analyst should also examine all evidence for feathers, insects or other bugs, plant material, pollen, or spores that are indicative of a location other than the incident site. These botanical pieces of evidence can be important for route interpretation. A tineid moth found in an interdicted sample (see Figure 14), for example, provided evidence of sample location between loss of legitimate control and interdiction.
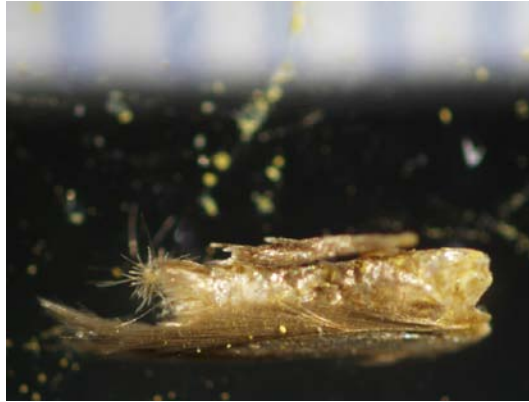
Figure 15

Optical photomicrograph of a tineid moth found in an
interdicted uranium powder sample. Reproduced
from (62).

Other Materials Evidence

Other associated evidence should be carefully examined for possible clues towards methods and route
interpretations. Such materials as glass, soil, dust, cosmetics, paints, inks & dyes, plastics, polymers,
metal objects (such as the staple shown in Figure 14), and tapes often vary in chemical composition
from place to place. Unique characteristics in these materials might tie the perpetrators to a specific
location, again a fact that can be important for route interpretation. In the same way, unique minerals
found on the evidence might be diagnostic of specific geology and location, i.e., geolocation.

Figure 16

A somewhat unusual staple found in an interdicted
uranium powder sample. Reproduced from (62).

Application & Sequencing of Techniques & Methods

The nuclear forensic scientist should, of course, consider issues such as specificity, sensitivity, detection
limit, precision, and accuracy in choosing an appropriate analytical method to apply to the nuclear
forensic sample. In addition, though, he must consider the cost of the analysis versus the benefit to be

derived from the results. Cost includes real financial cost, of course, the cost of both instrument time and the analyst's time, the cost of consumables used during the analyses, and so forth. However, cost should also include the "cost" of any sample consumed during analysis. In the case of non-destructive analysis (NDA), this cost may very well be zero, although one must always consider the potential of altering or contaminating the sample during NDA, rendering it useless for analysis by other techniques. In addition, if the amount of sample is quite large, this cost might be correspondingly quite small. Another potential cost might be time. For time-critical cases, the amount of time required for a specific analysis may be too long and the analyst should consider other techniques that can provide answers more quickly. When considering the benefit of an analysis, the analyst should first consider the relevance of the anticipated results. Relevance really reflects the connection between the anticipated results and signatures of interest. In the case of comparative signatures, do we have the necessary database or sample archive against which to compare our results? In the case of predictive signatures, do we have the necessary scientific insights to interpret the meaning of our results?

The ITWG has achieved a general consensus on the proper sequencing of techniques so as to provide the most valuable information as early as possible in the interpretation process. This consensus was achieved through discussion and consultation at regular meetings, as well as from experience developed from three round robin analyses by nuclear forensic laboratories. The collection of time or environmentally sensitive samples must occur within the first 24 hours after sample receipt. Non-destructive analysis should be conducted before destructive analyses whenever possible. Table 4 shows the generally accepted sequence of analysis, broken down into techniques that should be performed within 24 hours, 1 week, or 2 months.

Table 4

Sequence for Techniques/Methods

as determined by the ITWG (55).

Techniques/Methods	24 Hour	1 week	2 months
Radiological	Health & Safety assessment - Dose rate (α, γ, neutron) - Surface contamination - Radiography		
Physical Characterization	Preliminary - Visual inspection - Photography - Weight & dimensional determination - Optical microscopy - Density	Detailed (microstructure, morphology, etc) - SEM (EDX) - XRD	Detailed (nano-structure, morphology, etc) - TEM - EMPA
Classical Forensics	Initial - Assessment of presence and collection of classical forensic evidence		Detailed - Analysis and interpretation of classical forensic evidence
Isotope Analysis	Initial isotopic composition - Gamma spec on bulk material (i.e. is it HEU or not?)	Intermediate isotopic composition - HRGS - SIMS - TIMS - MC-ICP-MS - Alpha spec	Final isotopic composition - HRGS - SIMS - TIMS - MC-ICP-MS
	Initial Age Dating • HRGS Pu	Initial age dating - LA-ICP-MS	Age dating - HRGS - MC-ICP-MS - Alpha spec
Elemental/Chemical	Elemental / Chemical (may take longer) - XRF	Elemental / Chemical (may take longer) - ICP-MS - IDMS	

*All times above refer to time after receipt of sample(s) at the nuclear forensic laboratory.

Quality Assurance

From the law enforcement perspective, nuclear forensic results must meet the standards of evidence of the jurisdiction where the case is to be prosecuted.   In the United States, for example, the probative power and admissibility of scientific evidence in the courtroom has tended towards more restrictive interpretations of the Federal Rules of Evidence (36-37), a trend also reflected in the 2004 NRC study of bullet lead analysis and the subsequent withdrawal of this method by the FBI (63-65).   The Daubert Standard, for example, consists of four factors which a judge should consider when determining the admissibility of scientific evidence:

(1)   whether scientific evidence has been tested and the methodology with which it has been tested;
(2)   whether the evidence has been subjected to peer review or publication;
(3)   whether a potential rate of error is known; and
(4)   whether the evidence is generally accepted in the scientific community

The existence of a rigorous quality assurance system can help address several of these factors. According to the Quality Assurance Guidelines for Laboratories Performing Forensic Analyses of Radiological Materials (66):

> *"Quality Assurance is an integral part of a laboratory analysis program. It provides a means to deliver valid, traceable results, an ability to identify and correct anomalies, consistency from analysis to analysis within a given technique, between techniques and temporally, and assurance that errors will be minimal and stochastic. The QA program is the element of an analytical program that provides assurance in the results generated by the analyses. From a nuclear forensic perspective, a QA program ensures defensible and consistent input to the interpretation process in support of attribution assessments."*

Most forensic laboratories, including nuclear forensic laboratories, are seeking to accredit their quality assurance systems to the ISO 17025 standard (67). Both Lawrence Livermore National Laboratory and Savannah River National Laboratory have achieved accreditation by the American Association of Laboratory Analysis (A2LA) in the field of nuclear forensics, with several other laboratories in the process of obtaining such a certification. The ISO 17025 standard is based upon the essential structure of ISO 9000 with requirements in the following areas:

- Organization and management,
- Document control,
- Contracts and procurement,
- Corrective action,
- Control of records,
- Audits,
- Personnel qualifications and training,
- Facility infrastructure and security,

- Validation of methods, uncertainty, and measurement traceability,
- Equipment,
- Analytical procedures,
- Calibration and maintenance,
- Proficiency testing,
- Documentation and reporting,
- Sampling,
- Sample control,
- Safety, and
- Subcontracting services.

The critical components for the analytical measurements are the requirements to validate the analytical methods prior to use, to calibrate and maintain the analytical instruments, and to qualify and train the personnel who use the methods and instruments. The method for determination of uncertainty and the traceability of measurements is an important part of each method. Although adherence to the Guide to Uncertainty in Measurement (38) is not a requirement of ISO 17025, it has, in fact, become the standard for determining analytical uncertainty. Finally, ISO 17025 requires proficiency testing, which serves to exercise the entire quality assurance system and serves to ensure comparability of results from different laboratories.

As mentioned previously, although the quality assurance requirements for the admissibility of scientific evidence into a court of law may be rigorous, scientific results used for intelligence purposes have a need for similar quality assurance, although perhaps less formal than that required for law enforcement purposes.

Sampling

The quality of the analytical measurements is often limited by the quality of the sample. Uncertainties created in the field ripple through to uncertainties in the lab, etc. A thorough analysis of issues regarding operations at the incident site can be found in IAEA TECDOC-1313 (28) and the ITWG Guidelines for Evidence Collection in a Radiological or Nuclear Contaminated Crime Scene (68).

One must, of course, address issue of personnel and public safety first. Since traditional forensic evidence is frequently commingled with the radioactive evidence, the collection of forensic evidence must be consistent with good radiological safety practice. Limiting time in the contaminated area and maximizing distance and shielding between the exposed personnel and radioactive sources can lessen the risk to personnel. Appropriate personal protective equipment (PPE), e.g., rubber gloves, safety goggles, will be required. In cases where dispersible radioactive material is present, an approved respirator may also be needed.

Ill-considered collection of traditional evidence could compromise the radioactive material evidence and vice versa. Therefore, it is essential that appropriate thought be given to the manner and relative timing of traditional forensic evidence collection and radioactive material collection. Good communication

between nuclear forensic specialists and those responsible for collecting the evidence will help ensure that all factors are considered before a collection approach is adopted.

Finally, appropriate chain-of-custody procedures must be maintained during the evidence collection process. All evidence must be supervised and protected while awaiting transportation from the incident scene.

Conclusions

Nuclear forensics is an emerging discipline, driven primarily by national objectives, to include both those of law enforcement and national intelligence. Nuclear forensics is one input into nuclear attribution, in which responsibility is assigned, along with other source of information, such as law enforcement and intelligence. Nuclear forensics is used to generate technical conclusions by applying validated signatures to analytical results from the interdicted material. These validated signatures include both comparative signatures, in which the interdicted material is compared to the results from material of known origins, and predictive signatures, in which conclusions are generated without reference to other samples. Valid analytical results, in turn, depend on appropriately validated analytical methods, proper analytical sampling, and a quality control/assurance program.

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